



Excess lithium salt functions more than compensating for lithium loss when synthesizing $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ in alumina crucible



Kai Liu, Jiang-Tao Ma, Chang-An Wang*

State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- LLZTO pellets with different amount of excess Li_2CO_3 were prepared in Al_2O_3 crucible.
- Effect of excess Li_2CO_3 on property of LLZTO pellets was investigated systematically.
- Performance of Li-air batteries using LLZTO pellets as electrolytes was investigated.

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ABSTRACT

Garnet type electrolyte " $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ " (LLZTO) was prepared by conventional solid-state reaction in alumina crucibles and excess lithium salt (from 0% to 50 mol%) was added into the starting materials to investigate the effects of excess lithium salt on the property of LLZTO. SEM, XRD and AC impedance were used to determine the microstructure, phase formation and Li-ion conductivity. Cubic garnet with a minor second phase LiAlO_2 in the grain boundary was obtained for the pellets with excess lithium salt. As the amount of excess lithium salt increased, more Al element diffused from alumina crucibles to LLZTO pellets and reacted with excess lithium salt to form liquid $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ phase in the grain boundary, which accelerated the pellets' densification and reduced lithium loss at a high temperature. Ionic conductivity of LLZTO pellets increased with the amount of excess lithium salt added and leveled off at $\sim 4 \times 10^{-4} \text{ S cm}^{-1}$ when lithium salt exceeded 30 mol%. The performance of Li-air batteries with hybrid electrolytes, using homemade LLZTO thin pellets as solid electrolytes, was investigated. The LLZTO thin pellet with more excess lithium salt in starting material had a higher density and resulted in better cell performance.

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1. Introduction

Lithium ion solid electrolytes have been extensively researched in order to substitute for the flammable, volatile and relatively unstable organic liquid-based electrolytes, thus enhancing safety, reliability and endurance of Li-ion and lithium batteries, especially those of large-scale batteries [1,2]. Furthermore, high performance Li-air or Li-S batteries [3,4] can be made by fast lithium ion solid electrolytes. Garnet type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid electrolyte is one of the most promising electrolytes due to its high Li ion conductivity and chemical stability against Li metal anode [5,6]. In the synthesis of LLZO, an empirical excess amount of lithium salt is usually added to the starting materials, whose role is usually

considered as compensation for the lithium loss at elevated calcination temperatures [5–11]. We, however, think the excess lithium salt in the starting materials functions more than that for the following reasons:

- (1) In the synthesis of NASICON, the amount of excess lithium salt in starting materials significantly affects the ionic conductivity of the sintered NASICON pellets [12]. Excess lithium salt may have the same influence on the synthesis of LLZO.
- (2) The amount of lithium loss is uncertain, so the compensation is only qualitative. Different amount of excess lithium salt could cause different deviations of the stoichiometric lithium ratio, which may result in different concentrations of lithium ion and vacancy inside LLZO grains [13], and finally affect the crystal structure and ionic conductivity of LLZO.
- (3) It has been reported by several groups that Al contamination exists if alumina crucibles are used in LLZO synthesis, and the

* Corresponding author.

E-mail address: wangca@mail.tsinghua.edu.cn (C.-A. Wang).

amount of Al in LLZO has an influence on its sinterability [7] and ionic conductivity [8]. It is also suggested by Geiger et al. [9] that the use of lithium salt results in the production of a minor melt phase with dissolved Al_2O_3 from the crucible during sintering. Accordingly, it's reasonable to assume that the amount of lithium salt will affect the amount of dissolved Al_2O_3 in LLZO, which affects its properties.

- (4) A very recent research [10] demonstrated that introduction of Li_2O as an additive increases density of Ta doped LLZO (LLZTO) and improves ionic conductivity. Alumina crucibles were used in their work, and interaction between Li_2O and Al_2O_3 from the crucible was confirmed. During sintering, excess lithium salt in starting materials will decompose to form Li_2O , which plays the same role as Li_2O additive.

Therefore, when synthesizing high ionic conductive LLZO, especially in alumina crucibles, in addition to heat treatment and doping strategy, the amount of excess lithium salt in starting materials may be another important factor that should be noted. In this study, the heat treatment and doping strategy were both maintained unchanged throughout the process, in order to systematically investigate the effect of the excess amount of lithium salt in starting materials when preparing doped LLZO in alumina crucibles. This was simply done by measuring and comparing the structural and electrochemical properties of the doped LLZO pellets synthesized from starting materials with different amount of excess lithium salt added.

2. Experimental

Ta was chosen as the doping element for it can stabilize cubic garnet at room temperature and enhance ionic conductivity [14]. $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ samples with 0%, 10%, 20%, 30%, 40% and 50 mol% excess Lithium salt in starting materials (named LLZTO- $x\%\text{Li}_2\text{CO}_3$, where $x = 0, 10, 20, 30, 40$ and 50 , respectively) were prepared by solid-state reaction of stoichiometric amounts of Li_2CO_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%), La_2O_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%, dried at 900°C for 12 h), ZrO_2 (Aladdin, 99.99%) and Ta_2O_5 (Ourchem, 99.99%). The starting materials with different amount of excess Li_2CO_3 were fully ground with agate mortar and pestle, and then heated at 900°C for 6 h to decompose the metal salts. The resulting powders were fully ground again, pressed into pellets with a diameter of 10 mm and a thickness of ~ 1.8 mm under an axial pressure of 4 MPa, then annealed at 1140°C for 16 h in air while the pellets were covered with the same mother powder. For each sample, 5 pellets were prepared for counting. All the heat treatments were conducted in alumina crucibles ($>99\%$ Al_2O_3), covered by alumina lids. The interior diameter, depth and wall thickness of the alumina crucibles were 35 mm, 35 mm and 2.5 mm, respectively.

The density of the pellets was determined from the weight and physical dimensions. XRD (Bruker AXS D8 Advanced with Da Vinci) was used to monitor the phase formation. The microstructures of the pellets were examined using field-emission scanning electron microscope (Shimadzu SSX-550). Elemental distribution was investigated by energy dispersive X-ray detector (EDX, Oxford Instruments) equipped on the SEM. The elemental composition of the samples was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The impedance spectra were obtained with Au as electrodes which were sputter coated onto both parallel surfaces of the LLZTO pellets. An impedance analyzer (Agilent 4292A precision impedance analyzer) was used to carry out the measurement, and the applied frequency range was 40 Hz–100 MHz. Zview software was

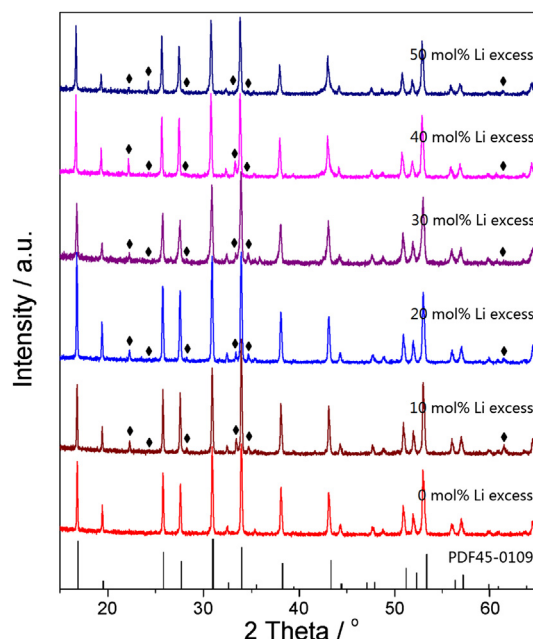


Fig. 1. Powder XRD result of grounded pellets sintered at 1140°C for 16 h. (\blacklozenge LiAlO_2 , PDF73-1338).

used to fit the impedance spectra and figure out the ionic conductivities of the samples.

3. Results and discussion

3.1. Phase and elemental composition

The XRD patterns of the powders heated at 900°C for 6 h are showed in Fig. S1. In this calcination process, the amount of excess Li_2CO_3 had a negligible impact on the phase of the samples. Fig. 1 shows XRD patterns of the LLZTO pellets sintered at 1140°C for 16 h. The XRD patterns matched well with the standard pattern known as cubic garnet phase $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (PDF45-0109), except for several minor peaks belongs to LiAlO_2 , indicating that cubic garnet was the major phase in all samples. These results suggested that excess lithium salt in starting materials was not crucial for formation of cubic garnet in LLZTO pellets. LiAlO_2 existed as a second phase in all the samples except for LLZTO-0% Li_2CO_3 . This

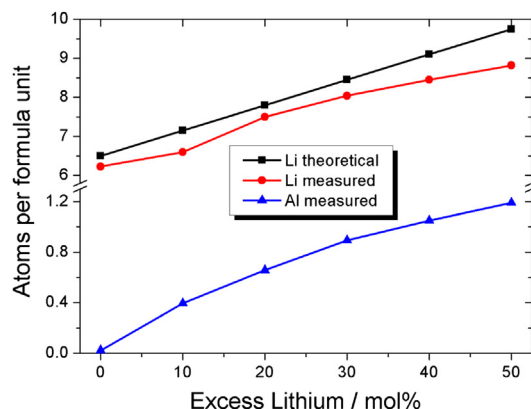


Fig. 2. Relationship between the amount of excess lithium and numbers of theoretical Li, measured Li and Al atoms per formula unit.

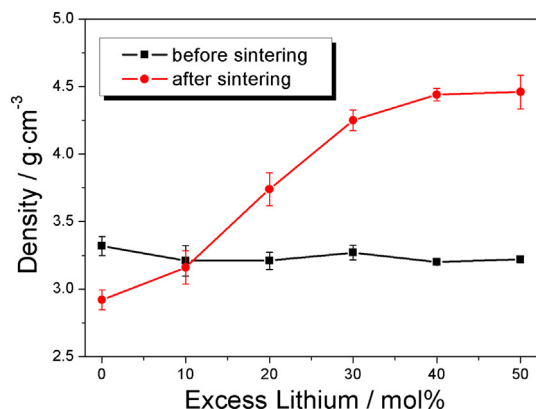


Fig. 3. Density evolution of the samples with different amounts of excess Li_2CO_3 .

phenomenon confirmed the interaction between excess Li_2CO_3 and alumina crucible, which formed $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ compounds.

The elemental compositions of the LLZTO pellets were measured by ICP-OES. The molar ratio of La:Zr:Ta in all the samples was approximately 3.0:1.5:0.5 (see Table S1), which was the ratio in the starting materials. In all the pellets, due to Li loss during sintering, the measured Li content was lower than the theoretical one, which was also reported in Ref. [11]. It is reasonable that numbers

of Li atoms increased with the amount of excess Li_2CO_3 , for the losses of Li element during sintering were at the same level, and more Li in starting materials resulted in more Li in the pellets. Interestingly, the numbers of Al atoms also increased with the amount of excess Li_2CO_3 , as showed in Fig. 2, which will be analyzed in Section 3.2. An increasing amount of excess lithium salt enhanced the interaction between lithium salt and alumina crucible, and altered the Al content in the samples, which affected the properties of the samples in turn, as described in the following sections.

3.2. Sinterability

With different amounts of excess Li_2CO_3 in starting materials, the samples exhibited different sinterability when sintered in alumina crucibles. Similar to the variation in linear shrinkage (see Fig. S2), density of the pellets increased with the amount of excess Li_2CO_3 . Above 30 mol%, the increase in density of the pellets became smaller, as Fig. 3 shows. Density of LLZTO-0% Li_2CO_3 decreased after sintering, and this could be explained by the loss of mass and unchanged dimensions (linear shrinkages were both ~ 0). A visual display of the pellets is given in Fig. S3.

SEM images of the pellets further confirmed the effect of excessive amount of lithium salt on the density of the pellets, as showed in Fig. 4. After being heated at 900 °C for 6 h and fully ground, the powders existed as micro-particles, and the particles

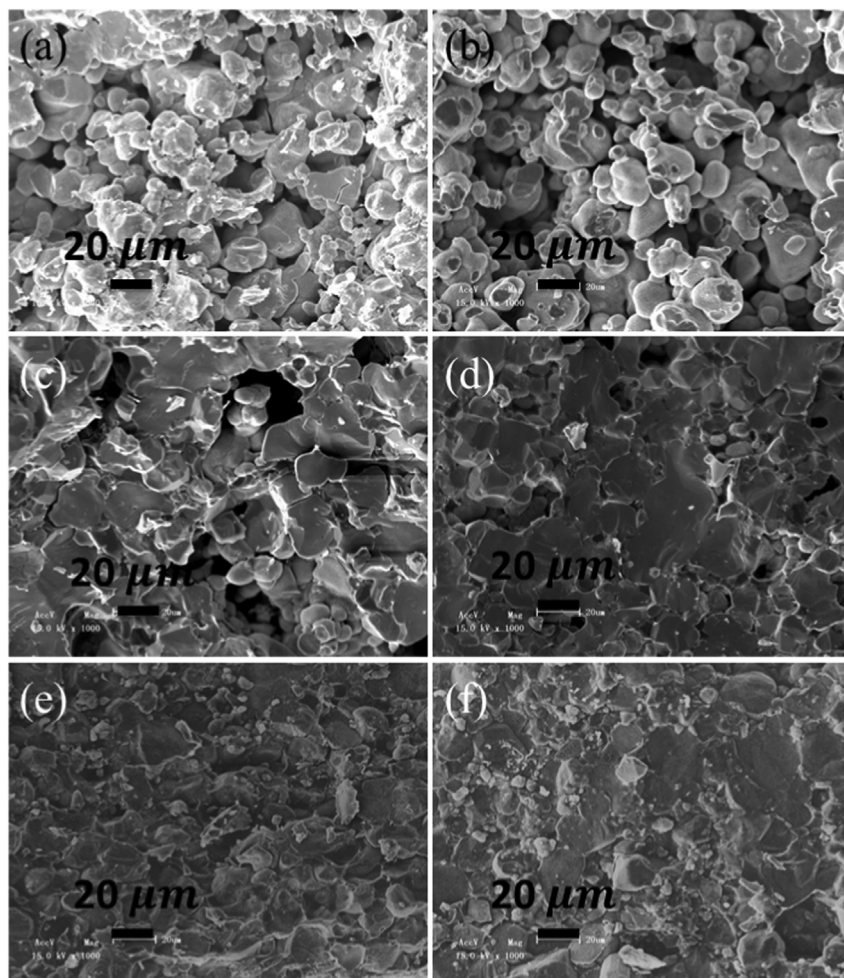


Fig. 4. SEM images of the pellets (fracture surfaces) after annealing at 1140 °C for 16 h. (a) $x = 0$; (b) $x = 10$; (c) $x = 20$; (d) $x = 30$; (e) $x = 40$; (f) $x = 50$.

bonded to each other after heat treatment at 1140 °C. As the amount of excess Li_2CO_3 increased from 0% to 50 mol%, connections between the particles became stronger, and the porosity of the pellet decreased. SEM images were in good accordance with the density results.

Larger amount of excess Li_2CO_3 resulted in better densification of the pellets. We supposed that the main reason for this phenomenon was the introduction of the Al element to the pellets, as well as the reaction between the Al element and excess Li element. Ying Jin and Paul J. McGinn [8] noted that Al additions promoted sintering of LLZO. They suggested that during sintering, reaction between Li_2O and Al_2O_3 formed a liquid phase, which was probably a eutectic liquid consisting of LiAlO_2 and Li_5AlO_4 , as can be seen in the Li_2O – Al_2O_3 phase diagram [15]. The formation of liquid phase enabled a liquid sintering, which accelerated densification. In our samples, SEM observations clearly showed the presences of a shell-like second phase wrapping the particles (Fig. 5(a)) and a fluid-like second phase existing at the intersection of the particles on the surface of the pellet (Fig. 5(b)). The fluid-like second phase could be evidence of the existence of liquid phase at high temperatures. Table 1 lists the composition of the particle and that of the second phase investigated by EDX. Al and La contents were much higher in the second phase than in the particle. These results agreed well with the results of Refs. [8,10]. Yutao Li et al. [14] also reported that most Al^{3+} from the alumina crucible were located in the grain boundaries in LLZTO pellet, and acted as a sintering aid. Therefore, it can be concluded that the excess lithium salt in starting materials

Table 1

EDX results of the points in the SEM image (all results in atomic %; – not detected).

| | Al | La | Zr | Ta | O |
|---------|-------|-------|------|------|-------|
| Point 1 | 1.46 | 19.41 | 4.89 | 0.91 | 73.33 |
| Point 2 | 15.69 | 4.33 | – | – | 79.98 |
| Point 3 | 1.26 | 18.04 | 4.27 | 0.79 | 75.64 |
| Point 4 | 17.03 | 3.84 | – | – | 79.13 |

reacts with Al_2O_3 in the crucible during sintering, inducing diffusion of Al^{3+} from the crucible to LLZTO pellet. The more excess lithium salt, the more Al^{3+} is introduced to the pellet, and most Al^{3+} is deposited at the intersection of the particles as a second phase, such as LiAlO_2 (observed in our samples), Li_5AlO_4 [8] and LaAlO_3 [8,13,16]. The amount of excess lithium salt determines the amount of dissolved Al_2O_3 from the crucible, which influences the formation of liquid phase during sintering, and finally affects the densification of LLZTO pellets.

3.3. Ionic conductivity

Fig. 6 displays typical room-temperature impedance plots of the sintered pellets with different amounts of excess Li_2CO_3 in starting materials. The total resistance (R_1) could be obtained by fitting the experimental data with the equivalent circuit [17] provided in the bottom right of Fig. 6. The total ionic conductivities of the pellets were determined from R_1 and physical dimensions. The results are summarized in Fig. 7. It can be found that, as the amount of excess Li_2CO_3 increased, the ionic conductivity significantly increased and then leveled off at $\sim 4 \times 10^{-4} \text{ S cm}^{-1}$. Since in all samples, the main phase was LLZO with cubic modification, and content of doping element, Ta, was the same, the difference of ionic conductivity could only be attributed to the difference of density and Al content of the pellets, which all arose from the different amounts of excess Li_2CO_3 . On the one hand, as the excess Li_2CO_3 amount increased, the variations in ionic conductivity (Fig. 7) and density (Fig. 3) were similar, indicating that the ionic conductivity was related to density. On the other hand, it is well known that Al content affects ionic conductivity of LLZO [8], and it is suggested that Al in LLZO plays two roles, i.e., doping element [9] and sintering aid [8]. Based on the above analysis, amount of excess lithium salt affects ionic conductivity of LLZTO by altering two factors: the density of LLZTO pellet and the level of Al content in LLZTO.

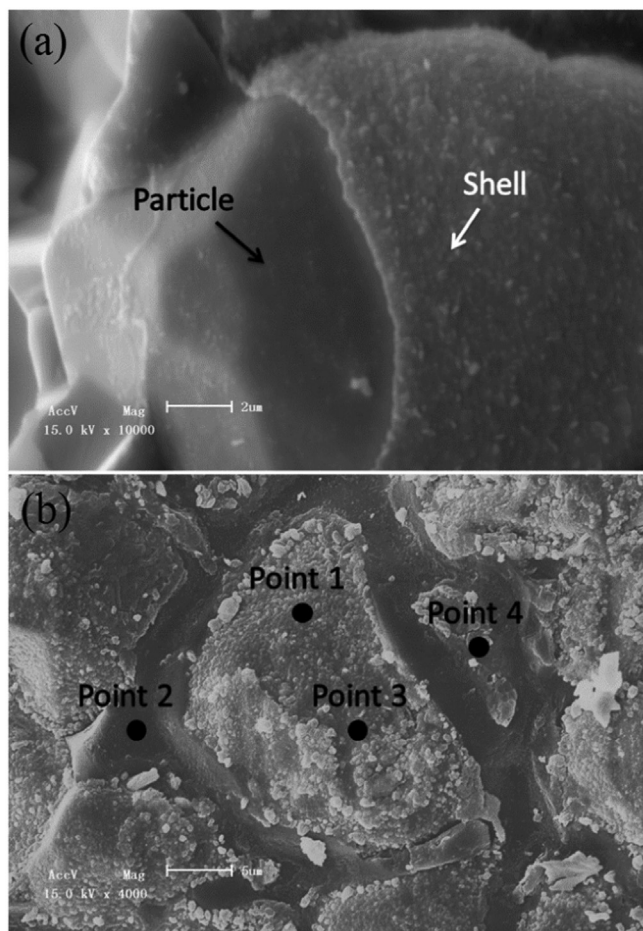


Fig. 5. SEM images of (a) fracture surface of sintered LLZTO–30% Li_2CO_3 pellet and (b) the surface of sintered LLZTO–50% Li_2CO_3 pellet.

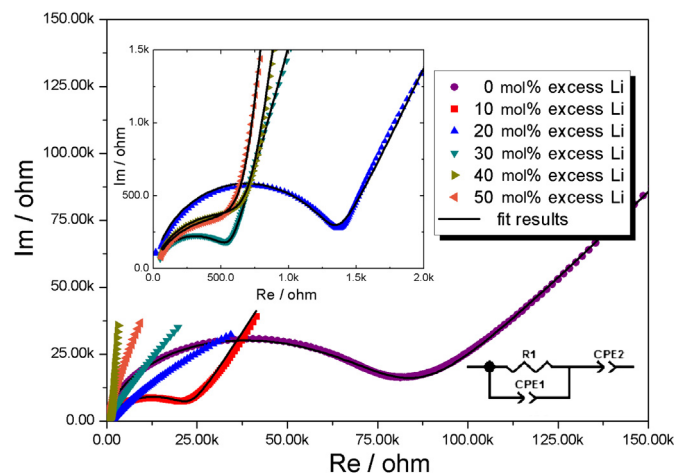


Fig. 6. Impedance plots (40 Hz–100 MHz) of the sintered pellets measured in air at room temperature.

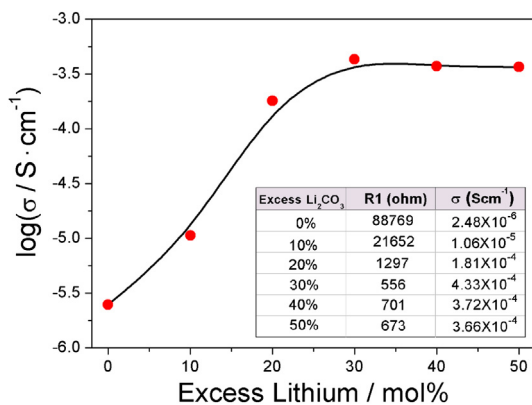


Fig. 7. Room-temperature conductivity of the sintered pellets with different amounts of excess Li₂CO₃ in starting materials.

3.4. Cell performance

To study application of the sintered LLZTO pellets in lithium battery, LLZTO–20%Li₂CO₃ and LLZTO–50%Li₂CO₃ pellets (LLZTO–0%Li₂CO₃ and LLZTO–10%Li₂CO₃ pellets were too porous to be thinned) were polished down to a thickness of ~150 μm and then used in a lithium-air battery with hybrid electrolytes (organic electrolyte in lithium side and aqueous electrolyte with dissolved O₂ in the other side, in between was the LLZTO thin pellet). The battery was discharged at a constant current density of 100 μA cm⁻². Fig. 8 shows the discharge curves. It can be seen that, when LLZTO–50%Li₂CO₃ thin pellet was used, the cell voltage was very stable, a flat discharging plateau at ~2.7 V was observed (curve (a)). However, the cell performance became much worse when LLZTO–20%Li₂CO₃ was employed, for the cell voltage fluctuated and fell down quickly. There was no obvious discharging plateau (curve (b)). The difference in cell performance could be mainly caused by the difference in densities of the LLZTO thin pellets. As shown in Fig. 4, the LLZTO–20%Li₂CO₃ pellet was much more porous, and Fig. 9(b) confirmed that, in the thin pellet, there were pores of different diameters, ranging from ~10 μm to ~50 μm. When the cell is in operation, water and organic electrolyte may seep through these pores, resulting in corrosion of lithium and decomposition of LiPF₆ in organic electrolyte, which made the cell performance unstable. However, the LLZTO–50%Li₂CO₃ was very dense (Figs. 4(f) and 9(a)) and pores could hardly be found. The penetration of the electrolytes was prevented, and the cell could therefore discharge stably.

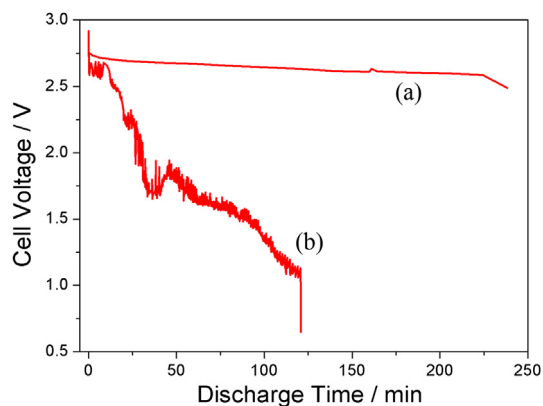


Fig. 8. Discharge curves of Li-air batteries with (a) LLZTO–50%Li₂CO₃ and (b) LLZTO–20%Li₂CO₃ thin pellet as solid electrolyte. Discharge at a constant current density of 100 μA cm⁻².

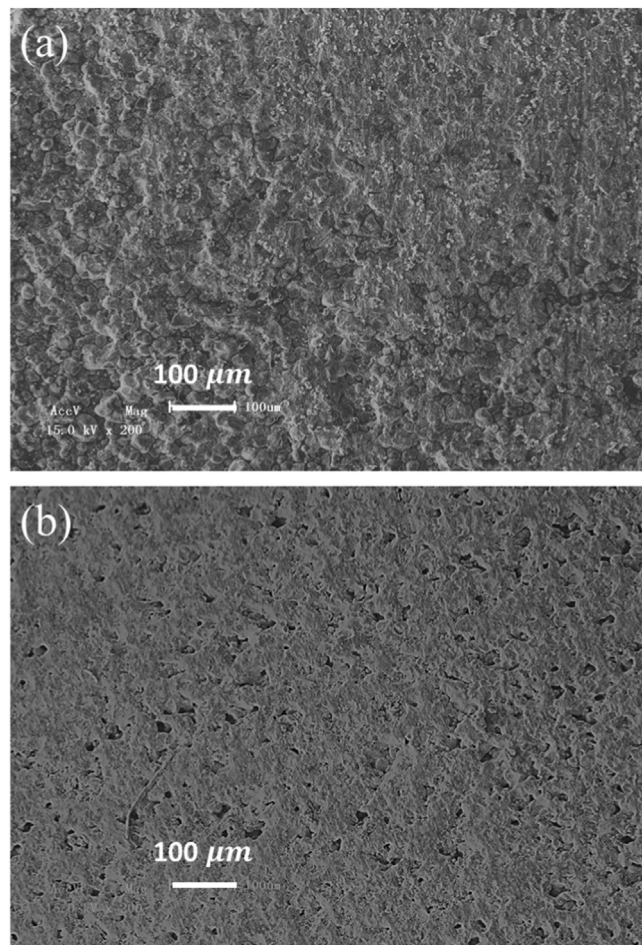


Fig. 9. SEM images for the surfaces of the (a) LLZTO–50%Li₂CO₃ and (b) LLZTO–20%Li₂CO₃ thin pellets after used in lithium-water battery.

Although ionic conductivities of the two thin pellets used in battery were on the same order, the thin pellet with low density performed much worse than the one with high density. It should be noted that besides its ionic conductivity, the relative density of the LLZTO pellet is also a critical factor in practical application. When synthesizing LLZTO in alumina crucible, the amount of excess lithium salt significantly affects the density, making it an important factor for consideration.

4. Conclusion

LLZTO pellets with different amounts of excess lithium salt (from 0% to 50 mol%) in starting materials were prepared and characterized. The major phase of all the sintered pellets was cubic garnet, and LiAlO₂ appeared as a second phase in all the pellets with excess lithium salt. Excess lithium salt interacted with the alumina crucible during sintering and induced Al³⁺ diffusion from the crucible to the LLZTO pellets. As the amount of excess lithium salt increased, Al content in sintered LLZTO pellets also increased. The contaminated Al element and the excess Li element reacted to form liquid phase at sintering temperature, improving densification of LLZTO pellets. Ionic conductivity of the LLZTO pellets increased with the amount of excess lithium salt and remained steady when excess lithium salt exceeded 30 mol%. Li-air batteries, using homemade LLZTO thin pellets as solid electrolytes, were assembled and tested. LLZTO thin pellet with more excess lithium salt in

starting material had a higher density and gave a better cell performance. In synthesizing LLZO or doped LLZO, especially in alumina crucibles, excess lithium salt functions more than compensation for Li loss, and its roles in affecting property of the product should be given greater consideration.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.02.065>.

References

- [1] J.W. Fergus, *J. Power Sources* 195 (2010) 4554–4569.
- [2] N.-S. Choi, Z. Chen, S.A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L.F. Nazar, J. Cho, P.G. Bruce, *Angew. Chem. Int. Ed.* 51 (2012) 9994–10024.
- [3] P.G. Bruce, L.J. Hardwick, K.M. Abraham, *MRS Bull.* 36 (2011) 506–512.
- [4] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nat. Mater.* 11 (2012) 19–29.
- [5] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* 46 (2007) 7778–7781.
- [6] M. Kotobuki, K. Kanamura, Y. Sato, T. Yoshida, *J. Power Sources* 196 (2011) 7750–7754.
- [7] A.A. Hubaud, D.J. Schroeder, B. Key, B.J. Ingram, F. Dogan, J.T. Vaughey, *J. Mater. Chem. A* 1 (2013) 8813–8818.
- [8] Y. Jin, P.J. McGinn, *J. Power Sources* 196 (2011) 8683–8687.
- [9] C.A. Geiger, E. Alekseev, B. Lazic, M. Fisch, T. Armbruster, R. Langner, M. Fechtelkord, N. Kim, T. Pettke, W. Weppner, *Inorg. Chem.* 50 (2011) 1089–1097.
- [10] Y. Li, Y. Cao, X. Guo, *Solid State Ionics* 253 (2013) 76–80.
- [11] M. Huang, T. Liu, Y. Deng, H. Geng, Y. Shen, Y. Lin, C.-W. Nan, *Solid State Ionics* 204–205 (2011) 41–45.
- [12] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G.-Y. Adachi, *J. Electrochem. Soc.* 140 (1993) 1827–1833.
- [13] E. Rangasamy, J. Wolfenstine, J. Sakamoto, *Solid State Ionics* 206 (2012) 28–32.
- [14] Y.-T. Li, J.-T. Han, C.-A. Wang, H. Xie, J.B. Goodenough, *J. Mater. Chem.* 22 (2012) 15357–15361.
- [15] L.P. Cook, E.R. Plante, *Ceram. Trans.* 27 (1992) 193–222.
- [16] Y. Shimonishi, A. Toda, T. Zhang, A. Hirano, N. Imanishi, O. Yamamoto, Y. Takeda, *Solid State Ionics* 183 (2011) 48–53.
- [17] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* 189 (2009) 371–377.